WILLIAM HERBERT HOBBS
University of Michigan
Ann Arbor, Mich.

Duplicate

REPRINT LIBRARY
Mineralogical Laboratory
University of Michigan
Gift of Professor W. H. Hobbs

THE BINARY SYSTEM

$Na_2Al_2Si_2O_8$ (Nephelite, Carnegieite) — $CaAl_2Si_2O_8$ (Anorthite).

BY

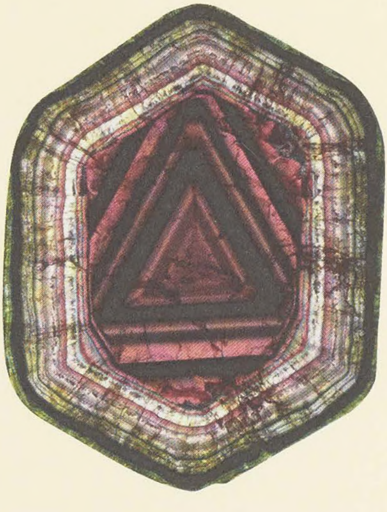
NORMAN LEVI BOWEN

ABSTRACT
OF
A THESIS

SUBMITTED TO THE FACULTY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

1912

RICHARD T. LIDDICOAT
COLLECTION



CONTENTS.

PAGE
INTRODUCTION 3
HEATING CURVES 4
  Results—Table I.
QUENCHINGS 4
  Results—Table II.
EXPLANATION OF SIGNS AND TERMS 7
  Equilibrium Diagram.
OPTICAL STUDY 9
  Properties of Anorthite.
    Carnegieite.
    Nephelite.
    Nephelite Mix-crystals.
APPLICATION TO NATURAL MINERALS 12
    Anorthite.
    Nephelite.
    Carnegieite.
THERMOMETRY 13
ACKNOWLEDGMENTS 14

GIA Library
The Robert Mouawad Campus
5345 Armada Drive
Carlsbad, CA 92008
(760) 603-4046

00013027

QE
389.62
.B68b
1912

THE BINARY SYSTEM:

$Na_2Al_2Si_2O_8$ (Nephelite, Carnegieite)-$CaAl_2Si_2O_8$ (Anorthite).

INTRODUCTION.

Of recent years there has been a continually growing demand among geologists for a precise knowledge of the thermal properties of minerals and mineral mixtures. With such data at hand, it is hoped that any inferences as to the processes whereby bodies of rock have attained their present condition in nature, will be more firmly grounded.

The experimental study here described, was undertaken with these facts in mind, and the results obtained may be regarded as a contribution to the desired data.

The work was carried on at the Geophysical Laboratory of the Carnegie Institution of Washington and the writer desires to express his thanks for the facilities afforded him there.

The system $Na_2Al_2Si_2O_8$-$CaAl_2Si_2O_8$ was chosen because of the very considerable importance of these compounds as rock-forming constituents.

The compound $CaAl_2Si_2O_8$ occurs in nature as the mineral anorthite. The preparation of anorthite in the laboratory has been accomplished by a number of workers.

The compound $Na_2Al_2Si_2O_8$ approximates in composition the natural mineral nephelite and has been prepared in a form resembling that of nephelite. It is mentioned in text-books of mineralogy as artificial soda-nephelite, and is given a place in order to bring out the chemical relationship within the hexagonal group of which nephelite is the best known member.

In the preparation of mixtures only specially purified materials were used and perfect homogeneity was insured by fusing and grinding alternately three times.

In a short preliminary study it was noted that all compositions crystallized readily; two different forms of the soda compound were observed, the one appearing at low temperatures (nephelite form), and the other at high temperatures (carnegieite form).

The lime compound was observed in only one form, anorthite.

HEATING CURVES.

With this amount of information it was possible to proceed with the exact determinations more expeditiously.

Small quantities of mixtures of various compositions were crystallized at a low temperature and heating curves run on each. The method employed was that found at the Geophysical Laboratory to be the best in mineral work. Descriptions of method and apparatus may be found in publications of the laboratory.[1]

In Table I the temperatures at which breaks were obtained on heating curves are given opposite the corresponding composition.

TABLE I.

Wt. $CaAl_2Si_2O_8$	Upper point.	Eutectic.	Inversion.	Knickpunkt.
0	1527°	—	1304°	—
0	1525	—	1305	—
10	1473	—	1335	1352°
10	—	—	—	1354
20	—	—	—	1360
20	—	—	—	1352
30	—	—	—	1349
40	—	1310°	—	—
50	—	1305	—	—
50	—	1304	—	—
60	—	1302	—	—
70	1437	1307	—	—
80	1484	1306	—	—
90	1522	—	—	—
100	1550	—	—	—
100	1549	—	—	—

QUENCHINGS.

In Table I there are many blanks. Doubtless, some of these could have been filled in by especially careful work with heating curves, but a different method was adopted for obtaining the same information.

The use of the quenching furnace, combined with the microscopic examination of the charges, is a trustworthy method of obtaining information as to the temperatures at which phases appear and disappear and, at the same time, a knowledge of the nature of the phases themselves[2]

A small charge of any mixture, wrapped in platinum foil, is held at a definite temperature for a length of time which is deemed sufficient to insure equilibrium for that temperature and composition, and is then quenched by allowing it to fall into a dish of mercury at room temperature.

---

[1] White, W. P., Amer. Jour. Sci., 4th ser., XXVIII, 1909, p. 453.

[2] Shepherd, E. S. and Rankin, G. A., Amer. Jour., Sci., XXVIII, 1909, p. 293.

The chilling is so sudden that any phase present at the furnace temperature is "fixed" and ready to be studied under the microscope. By running a series of quenchings, progress is made towards a knowledge of the phases present at equilibrium for each composition, at all temperatures; in short, towards the data necessary for an equilibrium diagram.

Several scores of quenchings were made. Of these, only the more significant will be tabulated (Table II), more especially those that determine the limits of stability for the various phases.

TABLE II.

Inversion.

No.	Composition. Wt. % $CaAl_2Si_2O_8$	Form at Start.	Temp.	Time.	Phases Found after Quenching.
1	0	Ne*	1245°	6 hrs.	Ne only
2	0	Ne	1252	1 hr.	Ne and Cg
3	0	Cg*	1245	1 hr.	Ne and Cg
4	0	Cg	1252	6 hrs.	Cg only
5	0	Glass	1260	1 hr.	Cg only
6	0	Glass	1252	1 hr.	Cg only
7	0	Glass	1245	1 hr.	Ne and Cg
8	0	Glass	1235	1 hr.	Ne and Cg
9	5	Ne	1260	4 hrs.	Ne only
10	5	Ne	1275	1 hr.	Ne and Cg
11	10	Glass	1317	7 hrs.	Cg and Ne
12	10	Ne	1282	4 hrs.	Ne only
13	10	Ne	1294	1 hr.	Ne and Cg (trace)
14	10	Ne	1296	1 hr.	Ne and Cg

Nephelite Solidus.

See also solid solution An in Ne.

No.	Composition. Wt. % $CaAl_2Si_2O_8$	Form at Start.	Temp.	Time.	Phases Found after Quenching.
15	20	Glass	1317°	7 hrs.	Ne only
16	20	Ne	1337	2 hrs.	Ne only
17	20	Ne	1340	1 hr.	Ne only
18	20	Ne	1343	1 hr.	Ne and glass
19	25	Glass	1328	1 hr.	Ne and glass
20	25	Glass	1322	1 hr.	Ne only
21	30	Glass	1310	2 hrs.	Ne only
22	30	Glass	1317	2 hrs.	Ne and glass

TABLE II.—*Continued.*

Nephelite Liquidus.

See also eutectic composition.

No.	Composition. Wt. % $CaAl_2Si_2O_8$	Form at Start.	Temp.	Time.	Phases Found after Quenching.
25	40	An[*] and Ne	1320°	1 hr.	Glass and Ne (bare trace)

Carnegieite Liquidus.

26	20	Glass	1412°	1 hr.	Glass and Cg (bare trace)
27		Glass	1417	1 hr.	Glass only
28	25	Glass	1374	1 hr.	Glass and Cg (rare)

Anorthite Liquidus.

30	50	An and Ne	1330°	1 hr.	Glass only
31	60	An and Ne	1380	1 hr.	Glass only
32	60	An and Ne	1392°	1 hr.	Glass only

Change of Phase at Knickpunkt.

33	3	Ne	1357°	6 hrs.	Cg only
34	5	Ne	1357	6 hrs.	Cg and glass trace
35	10	Ne	1357	6 hrs.	Cg and glass
36	20	Ne	1357	6 hrs.	Cg and glass
37	30	Ne	1357	6 hrs.	Glass only
38	3	Ne	1346	6 hrs.	Cg only
39	5	Ne	1346	6 hrs.	Cg and Ne
40	10	Ne	1346	6 hrs.	Cg and Ne
41	20	Ne	1346	6 hrs.	Ne and glass
42	30	Ne	1346	6 hrs.	Glass and Ne

Eutectic Composition.

43	50	Glass	1304°	2 hrs.	An and glass
44	40	Glass	1304	2 hrs.	Ne and glass
45	47.5	Glass	1304	1 hr.	An and glass
46	46	Glass	1304	1 hr.	An and glass
47	45	Glass	1304	1 hr.	Ne and glass

[*] Ne = Nephelite: Cg = Carnegieite; An = Anorthite.

TABLE II.—*Concluded.*

Solid Solution Anorthite in Nethelite.

No.	Composition. Wt. % $CaAl_2Si_2O_8$	Form at Start.	Temp.	Time.	Phases Found after Quenching.
48	30	Glass	1295°ca	2 days	Ne only
49	32	Glass	1295°ca	2 days	Ne only
50	35	Glass	1295°ca	2 days	Ne and An (mere trace)

Solid Solution Nephelite in Anorthite.

51	98.5	Glass	1250°	2 days	An only
52	98	Glass	1250	2 days	An and Ne (trace)
53	97	Glass	1290	2 hrs.	An and Ne

Solid Solution Anorthite in Carnegieite.

See also change of phase at knickpunkt.

54	3	Glass	1350	6 hrs.	Cg only
55	5	Glass	1350	6 hrs.	Cg and Ne (trace)

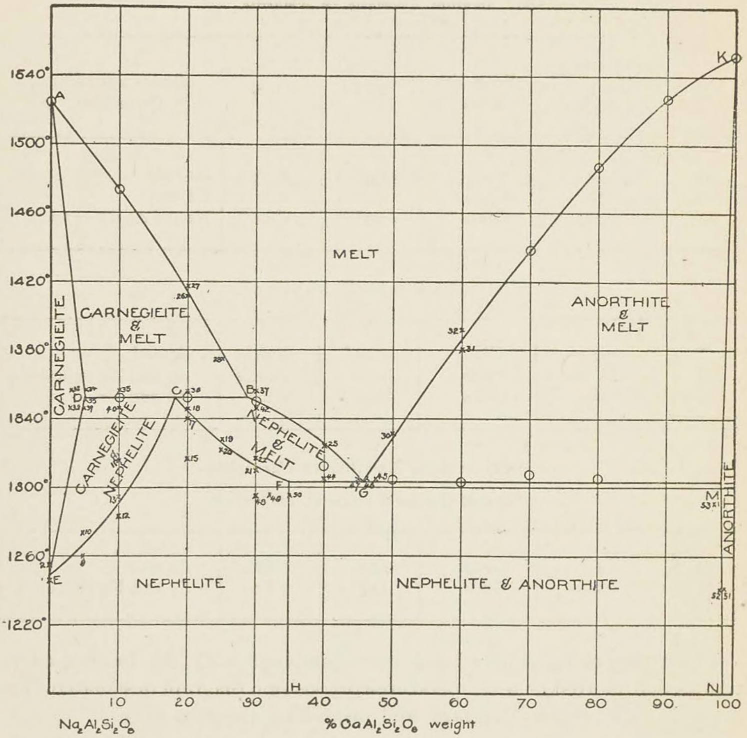
These quenching results have been combined with the heating-curve results and plotted on a temperature-composition diagram designated Diagram II, Equilibrium Diagram, and printed on the next page.

EXPLANATION OF SIGNS AND TERMS.

In Diagram II the circles indicate heating curve breaks; the numbered crosses indicate temperatures and compositions at which quenchings were made, the numbers corresponding with those in Table II, where the phases present are given. The data make possible the drawing in of the curves separating the fields of stability of the various phases. On each field the phases present at equilibrium are marked. Nephelite is used to indicate the hexagonal form of $NaAlSiO_4$ and also the isomorphous hexagonal mix-crystals with 0–35 per cent. $CaAl_2Si_2O_8$. Carnegieite is used to indicate the triclinic form of $NaAlSiO_4$ and also the isomorphous triclinic mix-crystals with 0–5 per cent. $CaAl_2Si_2O_8$. Anorthite indicates triclinic $CaAl_2Si_2O_8$ and also the isomorphous triclinic mix-crystals with 0–2 per cent. $NaAlSiO_4$.

Throughout the text abbreviations are used: Ne to indicate nephelite ($NaAlSiO_4$, hex.); Cg to indicate carnegieite ($NaAlSiO_4$, triclinic); An to indicate anorthite ($CaAl_2Si_2O_8$, triclinic). Nephelite mix-crystals are indicated, $Ne_{85}An_{15}$ or $Ne_{65}An_{35}$, the subscript numbers indicating the weight

DIAGRAM II. EQUILIBRIUM DIAGRAM.



percentage of $NaAlSiO_4$ and of $CaAl_2Si_2O_8$ present in the mix-crystal. Carnegieite mix-crystals are referred to in the following manner,—$Cg_{95}An_5$ and anorthite mix-crystals,—$An_{98}Ne_2$. $NaAlSiO_4$ and $Na_2Al_2Si_2O_8$ are used interchangeably. The purpose in using the latter form is that of bringing out clearly the analogy between the two components; no knowledge of the molecular weight is implied. Diagram II is the only diagram here contained on which certain points are lettered, and when these points are referred to by letter in the text, it has not always been considered necessary to specify Diagram II.

Only brief mention of a few of the features of the diagram can be made in this abstract; the experimental detail is, of necessity, omitted.

The compound $Na_2Al_2Si_2O_8$ crystallizes below 1248° in the hexagonal form, nephelite; at 1248° this form inverts to the triclinic form, carnegieite, which melts at 1526°. Anorthite melts at 1550°.

The low temperature form of the soda-compound (nephelite) is capable of holding 35 per cent. of the lime compound in solid solution. The inversion temperature experiences a sharp rise as the lime molecule is taken into solid solution.

Carnegieite can hold a maximum of but 5 per cent. $CaAl_2Si_2O_8$ in solid solution.

A eutectic point occurs at 1302° between nephelite solid solution (Ne_{65}-An_{35}) and anorthite, the composition of the eutectic mixture being, $CaAl_2Si_2O_8$ 45.5 per cent., $Na_2Al_2Si_2O_8$ 54.5 per cent. (weight).

Another triple point (Knickpunkt) occurs at 1352°, at which temperature carnegieite ($Cg_{95}An_5$) and nephelite ($Ne_{82}An_{18}$) are in equilibrium with a liquid with 28.5 per cent. $CaAl_2Si_2O_8$.

OPTICAL STUDY.

In the microscopic examination of the product of each experiment the method employed for identifying constituents was that of determining refractive indices in the crushed grains, by immersion in liquids of known index. This method is especially useful for the detecting of small quantities of any component. If the preparation be placed in a liquid which matches the mean index of the excess constituent, even very minute quantities of another constituent show up markedly, except in the rare case of different substances with nearly identical refractive indices. Moreover, it is possible to determine in the crushed grains most of the properties by which minerals are identified in thin section, such as order of birefringence, optical character, etc.

Anorthite.

The optical properties of anorthite had previously been determined in detail at the Geophysical Laboratory by H. E. Merwin and the figures given are the results of his work.

$$\alpha = 1.576, \quad \gamma = 1.589, \quad \gamma - \alpha = .013, \quad 2V = 80° \pm 3°, \quad \beta = 1.583, \quad G = 2.765.$$

Carnegieite.

Carnegieite always shows polysynthetic twinning similar to that in albite, with high extinction, up to 36°, against the twinning lines. Other less persistent twinning lamellae appear crossing these at various angles, often giving a microcline-like structure. On account of the universal intricate twinning, many of the optical properties are difficult of determination. The indices, obtained by matching with a liquid in sodium light, and then determining the index of the liquid on the Abbé refractometer, gave

$$\gamma = 1.514, \quad \alpha = 1.509, \quad \gamma - \alpha = .005.$$

The mean index is therefore low, comparable with that of leucite. The birefringence, measured with the compensating quartz wedge,[1] gave

---

[1] Wright, F. E., Amer. Jour. Sci., 4th ser., XXVI, 1908, p. 349.

.0052 and .0048 in different plates. Optical character negative, 2V small, 12°–15°, probably triclinic.

All efforts to obtain euhedral crystals failed. In all charges showing carnegieite and glass (area ADB), the carnegieite is always in rounded crystaline globules. An attempt to grow crystals in a flux gave nothing but similar globules.

The density of crystalline carnegieite is 2.513 at 21°, determined in Thoulet's solution, on carefully selected material free from air bubbles.

Nephelite.

In all charges consisting of nephelite and glass (area CBGF), the nephelite shows under the microscope in perfect hexagonal basal sections, or rectangular prismatic sections, indicating the hexagonal nature of these mix-crystals.

Of the pure sodium compound, nephelite, euhedral crystals were prepared in sodium tungstate over a Bunsen burner. These were always bounded by the prism and terminated only by the base. One of these was measured on the two-circle reflecting goniometer and the hexagonal nature confirmed. The maximum deviation from 60° of the measured prism angle was 16′, and the average deviation 8′, with fair to good signals. The indices, determined by the immersion method in sodium light, gave ω = 1.537, ε =1.533. Birefringence .004, slightly but noticeably less than that in carnegieite.

About half a gram of these crystals was tested for tungstic acid by boiling with hydrochloric acid. Only pure white silica was left, with no yellow tinge. The amount of tungstic acid could not have been more than a trace.

The density of these crystals is 2.619 at 21°. The degree of correspondence of the artificial compound with the natural mineral is shown in the following table:

	Crystallization.	Optical Character.	ω.	ϵ.	Sp. G.	Crystal Habit.
$NaAlSiO_4$ (artificial)	Hexagonal	Negative	1.537	1.533	2.619	Prism and base
Nephelite (natural)	Hexagonal	Negative	1.541	1.537	2.55–2.65	Prism and base predominant.

It may be fortuitous that there is close correspondence with Gladstone's law in the relation between the mean indices and densities of the two forms of the soda compound, but the fact is, perhaps, worthy of note. Gladstone's law states that the specific refractive energy $\frac{n-1}{d}$ is constant, whatever the state of the molecular aggregation.

We have then

$$\text{for carnegieite } \frac{1.512-1}{2.513} = .2037.$$

$$\text{for nephelite } \frac{1.535-1}{2.619} = .2042.$$

Nephelite Mix-crystals.

It was found possible to determine definitely the variation, with composition, of the optical properties of the hexagonal mix-crystals or solid solutions from Ne to $Ne_{65}An_{35}$. With increasing proportion of the lime molecule the birefringence of .004 (negative) grows less passes through zero and finally becomes .002 (positive).

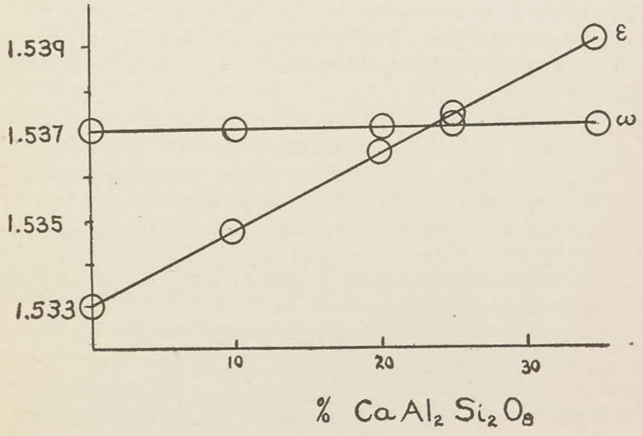
The indices were determined in sodium light at room temperature by the immersion method. The results are shown in Table III and in the plot, Diagram III.

TABLE III.

INDICES OF REFRACTION OF NEPHELITE MIX-CRYSTALS.

% $CaAl_2Si_2O_8$	ω.	ε.	Birefringence.	Optical Character.
0	1.537	1.533	.004	—
10	1.537	1.535	.002	—
20	1.537	1.537—	Very weak	—
23	1.537	1.537	None	Isotropic
25	1.537	1.537+	Very weak	+
35	1.537	1.539	.002	+

DIAGRAM III.



It will be noted that the index of the ordinary ray remains sensibly constant, while that of the extraordinary ray mounts from 1.533 to 1.539. At the composition $Ne_{77}An_{23}$ (approx.), we have the unique case of hexagonal crystals isotropic with respect to sodium light.

APPLICATION TO NATURAL MINERALS.

Anorthite.

Several natural anorthites approximate closely to the theoretical composition. The melting points of some of these have been determined. Brun[1], working with Seger cones, and Douglas[2], the latest worker with the meldometer, have obtained figures that differ comparatively little from the figure given by Day and Sosman for pure anorthite (1550°).

Anorthite from Idsu, Japan, 1490–1520—Brun.

Anorthite from Mte. Somma, 1505—Douglas.

Nephelite.

In a recent paper[3] the writer has shown that experimental results are in accord with Schaller's statement that natural nephelites may be regarded as solid solutions of the three molecules $NaAlSiO_4$, $KAlSiO_4$ and $NaAlSi_3O_8$.

Natural nephelites, then, differ considerably in composition from the compound $NaAlSiO_4$ used in this work, and the difference in thermal properties is correspondingly great. Thus, it was found by the writer that nephelite from Magnet Cove, quenched from 1370°, gave only a clear glass and therefore melts at some temperatures below 1370°. Moreover, Wright§ has found that molten 'nephelite' (Magnet Cove) crystallizes directly as nephelite without first showing the carnegieite form. In this respect nephelite from Magnet Cove behaves like the artificial nephelite with 28.5–35 per cent. $CaAl_2Si_2O_8$ in solid solution.

That nephelite will hold 35 per cent. anorthite in solid solution, whereas carnegieite, which, like anorthite, is triclinic, will hold at most 5 per cent. comes rather as a surprise. That miscibility in the solid state does not always follow from crystallographic similarity is, however, well exemplified in a number of cases.

The very limited solubility of $Na_2Al_2Si_2O_8$ in anorthite has some importance in the light of the Linosa feldspar of abnormal composition recently described by Washington and Wright.[4] These writers came to the decision that the composition of the feldspar might be written $Ab_8An_{10}Cg_1$. The writer has found that solid solution of Ne (Cg) in anorthite extends only up to 2 per cent., while, if the explanation of the Linosa feldspar offered by Washington and Wright is correct, solid solution of Ne in the plagioclase Ab_8An_{10} extends to 5.5 per cent.

---

[1] Brün, A., Arch. sci. phys. et nat., 4th ser., XIII, 1902, p. 352.

[2] Douglas, J. A., Quart. Jour. Geol. Soc. London, 1907, p. 145.

[3] Bowen, N. L., Amer. Jour. Sci., 4th ser., XXXIII, 1912, p. 49.

[4] Washington, H. S. and Wright, F. E., Amer. Jour. Sci., 4th ser., XXVI, 1908, p. 349.

Carnegieite.

The mineral carnegieite has never been definitely identified in nature. Most natural nephelites probably crystallized as such, for, if formed by inversion from carnegieite, the crystals would be unlikely to show continuous orientation.

In order that carnegieite might occur in a rock it is necessary that its crytallization should have taken place at a temperature above that at which the crystal form would change to that of nephelite, otherwise nephelite would occur. The inversion temperature 1248° applies only to the pure compound, $NaAlSiO_4$. The presence of other substances affects this inversion point only when those substances can be taken into solid solution by the nephelite or carnegieite. In this work the effect of anorthite has been determined, and is such that crystallization would have to occur at a temperature still higher than 1248°, in order that carnegieite might form, the maximum raising being about 100°.

The effect of the other substances which nephelite is capable of holding in solid solution is, however, still unknown, but the evidence is that the aggregate effect is not sufficient to carry the inversion point below the temperature at which the crystallization of nephelite from most rock magmas would begin, otherwise carnegieite would be common.

From certain magmas very rich in 'nephelite,' the crystallization of carnegieite might be expected, but even this statement needs qualification, for as we have seen some nephelite, viz. that from Magnet Cove, may crystallize from its own melt directly as nephelite.

E. Esch describes an abnormal nephelite from the nephelinite of Etinde volcano in German Kamerun.[1] This mineral shows inclined extinction and a complicated twinning and is biaxial. In these properties it agrees better with carnegieite than with nephelite. On the other hand, the crystal outline is like that of nephelite and the determined mean index, 1.5376, very close to that of nephelite, but such an index is not impossible in carnegieite with certain compounds in solid solution. The mineral may possibly be carnegieite but no definite decision can be arrived at until the possibilities of solid solution in carnegieite have been further investigated. This single instance appears to be the only one in which a mineral whose properties suggest carnegieite, has been described.

THERMOMETRY.

In the fact of its non-appearance in nature carnegieite is like a great many other allotropic forms of minerals that have been made in the laboratory. These modifications are, in nearly all cases, the high temperature forms, and their absence constitutes one of the proofs of the prevailingly low temperatures of natural magmas during crystallization. It is evident from the

[1] Esch, E., Sitzb. Berl. Akad., XVIII, 1901, 400.

discussion in the preceding paragraph that care must be exercised in putting to use the inversion of nephelite on the geologic thermometer scale.[1]

Minerals of simple, definite composition, SiO_2, $CaSiO_3$, and others, have definite inversion points and the limits of stability of each form give definite points on the scale. A mineral of variable composition has a temperature of inversion which varies conjointly. With known composition, however, it will be possible when sufficient experimental data has accumulated to set equally definite limits to its stability as is exemplified in the present case of nephelite with variable content of lime.

There is reason to believe, as formerly pointed out, that natural nephelites first crystallized as such.

In the event of the discovery of a natural carnegieite its crystallization above 1200°[2] could be asserted with but little fear of error.

The writer is indebted to E. S. Shepherd and F. E. Wright of the Geophysical Laboratory for much help and advice throughout the course of the experimental work.

---

[1] Wright, F. E. and Larsen, E. S., Amer. Jour. Sci., XXVII, 1909, p. 421.

[2] It is necessary to leave some margin for a possible lowering due to solid solution.

R-5-12—300.

GIA Library
The Robert Mouawad Campus
5345 Armada Drive
Carlsbad, CA 92008
(760) 603-4046

DATE DUE

GAYLORD
PRINTED IN U.S.A.

Gemological Institute of America
00013027
Library